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Lightweight Fibrous Nickel Electrodes for Nickel-Hydrogen Batteries

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ELECTRODES FOR NICKEL-HYDROGEN BATTERIES
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Doris L. Britton
Lewis Research Center
Cleveland, Ohio

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LIGHTWEIGHT FIBROUS NICKEL ELECTRODES FOR NICKEL-HYDROGEN BATTERIES

Doris L. Britton
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

The NASA Lewis Research Center is currently developing nickel electrodes for nickel-hydrogen batteries. These electrodes are lighter in weight and have higher energy densities than the heavier state-of-the-art sintered nickel electrodes.

Lightweight fibrous materials or plaques are used as conductive supports for the nickel hydroxide active material. These materials are commercial products that are fabricated into nickel electrodes by electrochemically impregnating them with active material. Evaluation is performed in half cells structured in the bipolar configuration. Initial performance tests include capacity measurements at five discharge levels, C/2, 1.0C, 1.37C, 2.0C, and 2.74C. The electrodes that pass the initial tests are life cycle-tested in a low Earth orbit regime at 80 percent depth of discharge.

INTRODUCTION

The NASA Lewis Research Center is currently involved in the development and design of nickel hydrogen (Ni-H₂) cells and batteries primarily for low-Earth-orbit (LEO) applications. These designs have been incorporated into both the individual pressure vessel (IPV) cells as well as bipolar batteries using active cooling. The objective of this program is to improve the life, performance, and energy density of Ni-H₂ devices when cycled under a LEO regime at deep depths of discharge.

One important aspect for this improvement is to develop a better and lighter weight nickel electrode which, in addition to being identified as the critical component, has also been identified as the heaviest component of the Ni-H₂ battery system. The SOA nickel plaque is made by sintering fine nickel powder onto a wire screen at elevated temperature (1000 °C) in a reducing atmosphere. This plaque has the advantage of providing a highly conductive and porous substrate for the active material but has the disadvantage of being heavy in weight. The nickel hydroxide active material is deposited into the pores of the plaque either by chemical or electrochemical methods.

EXPERIMENTAL

Nickel Plaque

The use of a lightweight nickel plaque in place of the heavy sintered nickel plaque is expected to lead to improvements in energy density, weight, cost, and performance of the nickel electrode. After some preliminary experiments, nickel fiber plaques were selected as a promising support candidate for

the Ni(OH)_2 active material. The fiber materials tested were the Fibrex fiber mat from National Standard, the Metapore nickel felt from Sorapec, and a machined sintered nickel fiber mat from Nippon Seisen (Japan). The relative weights of the fibrous electrodes compared with the SOA sintered electrode is shown in figure 1. A reduction of about 40 percent in nickel electrode weight is possible by replacing the heavy sintered plaque with the lightweight plaques.

The lightweight nickel electrode cycle life test was initiated using the Fibrex nickel fibers from National Standard Co. These materials are formed by reducing and sintering fibers extruded from a mixture of nickel oxide and binding agents (ref. 1). A special type of Fibrex mat that is layered with carbonyl nickel powder is currently being tested. This special type of material contains a 50:50 ratio of nickel fiber to nickel powder with 86 percent porosity, 30 mil thickness, and a density of 95 mg/cm^2 .

Electrodes made from porous lightweight mats have a common feature of exhibiting a low initial utilization which gradually increases with cycling. This was observed in earlier work on the nickel plated plastic at NASA Lewis (ref. 2) and the nickel composite electrode at Naval Surface Weapons Center (ref. 3). W. Lee (ref. 4) reported that the addition of cobalt hydroxide $[\text{Co(OH)}_2]$ to the impregnated electrode will help to achieve full utilization of the Ni(OH)_2 active material earlier during cycling than in the untreated electrode. In an attempt to eliminate this added step, a special Fibrex material containing 50 percent nickel fiber, 35 percent nickel and 15 percent cobalt powder was prepared by National Standard. This special material has similar porosity, thickness, and density as the original Co powder-free substrate.

Electrochemical Impregnation

The substrates are electrochemically impregnated in an aqueous bath containing $1.5\text{M Ni(NO}_3)_2$, $0.175\text{M Co(NO}_3)_2$, and 0.075M NaNO_2 made acidic by the addition of 50 percent nitric acid (ref. 5). The bath is maintained at a constant temperature of 95 to 100°C and a pH of 3 to 4.

The plaques are impregnated for various periods of time (2 to 5 hr) and current densities (50 to 93 mA/cm^2) to determine the conditions needed to obtain the optimum loading level. The plaques are impregnated in a reaction vessel which consists of a 600 ml beaker containing 300 ml of the aqueous nickel nitrate impregnation solution. The plaques are placed between two standard nickel counterelectrodes in a Teflon holder.

After washing the impregnated plaques, the electrodes are formed using the Eagle-Picher procedure (ref. 6) which consists of eight cycles of 20 min charge and 20 min discharge at approximately 3C rate. After formation, the electrodes are thoroughly rinsed in deionized water, dried at a temperature of 60°C for 4 hr and weighed. The theoretical capacity is determined from the weight of the active material in the electrode using the electrochemical equivalent of 0.289 A-hr/g of Ni(OH)_2 .

Cycle Life

The cycling tests are continuous cycling in a LEO regime (55 min charge, 35 min discharge) at 80 percent depth-of-discharge. The voltage as a function of time is plotted continuously. Approximately every 1000 cycles, capacity measurements are made by discharging to -0.2 V (versus a Hg/HgO reference electrode) at a 1.37C rate after charging for 80 min at a C rate. The percent utilization of the electrode is calculated by using the ratio of the measured capacity to the theoretical calculated capacity based on the weight of the active material deposited. End of life or failure is defined as the point where the discharge voltage degrades to -0.2 V versus a Hg/HgO electrode.

Electrode Performance

The electrode performance at different cycles is measured at five discharge levels, C/2, 1.0C, 1.37C, 2.0C, and 2.74C rates. The voltage as a function of time and the capacities at each rate are recorded and compared with sintered nickel electrode and other experimental electrodes.

Pore Size Distribution

Pore distribution and porosity of nickel fiber plaques, new and cycled nickel electrodes are measured using mercury intrusion porosimeter method.

RESULTS AND DISCUSSION

Electrochemical Impregnation

For the Fibrex fiber mat, a constant current density of 77.5 mA/cm² for 4 hr gave a loading level of active material of 1.6 g/cm³ void. The 1.6 g/cm³ void was selected as the optimum loading level because the cycle life has been found to maximize at this value when SOA sintered plaques are used (ref. 7). This value will vary when lightweight plaques are used but for now, the 1.6 g/cm³ value will be used in order to compare the results with the existing data on the SOA sintered nickel electrodes with similar loading levels. A 13 percent increase in thickness was measured when loading the Fibrex mats at this level. For comparison, an increase of less than 5 percent was observed when loading the SOA sintered plaque at the same level. The active material loading level of the Fibrex electrode was calculated using the expanded electrode thickness. The log-log plot of loading level versus percent thickness expansion is shown in figure 2. The electrode thickness increases as the loading level increases. This straight line plot has a least square intercept of 0.94 and a slope of 1.1. This thickness expansion is quantitatively related to the loading level by the following equation:

$$\log (\text{percent thickness expansion}) = 1.1 \log (\text{loading level}) + 0.94 \quad (1)$$

Cycle Life

The cycle life data of the Fibrex nickel electrode is shown in figure 3. The maximum utilization of the nickel electrode can exceed 100 percent since the valence change of the nickel ions during charge and discharge can be greater than 1 and the percent utilization values in this report are calculated based on a nickel ion valence change of 1. The utilization of the Fibrex electrode shows a region of increasing rate during the initial 100 cycles followed by a relatively constant plateau region to 2800 cycles. A gradual performance decrease is then observed as the number of cycles is further increased.

The Fibrex nickel electrode cycled for 4534 cycles before it reached its end of life. The capacity of this electrode had decreased by 25 percent by the end of the cycle test. The thickness of the electrode measured after the cycle life test showed an increase of about 8 percent over the initial electrode thickness measured after the impregnation process. For comparison, the thickness of the SOA sintered electrode expanded to about 10 percent after 4500 cycles (ref. 7).

Electrode Performance

The discharge voltage versus time of the Fibrex electrode as compared with the standard Eagle-Picher electrode, at the beginning of the life cycle test, is shown in figure 4. A higher voltage curve and longer discharge time at the same 1.37C discharge rate was obtained with the experimental nickel electrode.

Figure 5 shows the utilization data of the Fibrex nickel electrode at the different discharge rates. The results indicate that as the electrode cycles, the utilization decreased as the discharge rate increased. The electrode utilizations depended on the discharge rate and showed lower results at the higher rate. The initial measurement of the electrode utilization is about 3 percent smaller at the 2.74C discharge rate than at the C/2 rate. After 3000 cycles, the utilization at the 2.74C discharge rate is 20 percent less than at the C/2 rate. At the low discharge rate of C/2 though, the utilization after 3000 cycles is about the same as the initial data. There is no sign of any deterioration in the low rate capacity with cycling. The failure of the electrode appears to be due to the loss of high rate discharge capacity rather than the loss in total electrode capacity.

Pore Size Distribution

Figure 6 shows the pore size distribution of the lightweight plaques compared to the standard sintered plaque. All of the fibrous plaques have larger pore radii than the Eagle-Picher SOA sintered plaque. The nickel felt mat from Sorapac has the largest incremental volume of about 0.3 cc/g at the pore radius of 60 μm . The Nippon Seisen fiber mat has its peak at 90 μm . The Fibrex fiber mat from National Standard exhibits the broadest distribution of pores at about 11 to 60 μm . The Eagle-Picher sintered plaque has its peak at about 14 μm .

As was mentioned earlier, electrodes made from porous lightweight plaques exhibit a low initial utilization which gradually increases during cycling. This phenomenon maybe attributed to the large pore sizes of the plaques.

Besides having larger pore sizes, the lightweight plaques also have a wider range of pore diameters and a more irregular pore shape than the SOA plaque. The initial utilization of the electrodes made from the nickel fiber mats from National Standard, Sorapec, and Nippon Seisen is about 50 to 60 percent of the theoretical capacity. In comparison, the initial utilization of the electrode made from the SOA sintered plaque is about 90 percent.

Figure 7 shows the pore size distribution curves of the Fibrex electrode. Cycling to failure increases the total pore volume which is probably due to the expansion of the electrode. The pore size distribution of the Fibrex electrode shows a distinct multiple peak profile from 0.01 to 10 μm as opposed to the minimal peak profile of the SOA electrode across the same region as shown in figure (8) (ref. 8). There is a definite shift in the average pore size and distribution of the cycled SOA electrode toward smaller pores. The peaks at 0.7, 2, and in the range greater than 7 μm decrease while the peak at 0.01 μm increases in size and slightly shifts to the right. The shift to smaller pores and increase in volume requirements of the SOA electrode result in the electrode having a greater affinity for electrolyte. This effect can dry the separator and will lead to a high separator resistance. This traditional increase in small pores of the cycled SOA electrode is not found in the Fibrex electrode. In addition to a two-fold increase in volume of the micropores of the cycled Fibrex electrode, the volume of the larger pores (over 9 μm) increases 2 to 4 times. The pore size distribution curve of the cycled Fibrex electrode should not result in the electrode competing with the separator for electrolyte because of its bimodal pore size distribution.

CONCLUSIONS

Fabrication and life cycle testing of lightweight fiber nickel electrodes have demonstrated the feasibility of an improved and higher energy density nickel electrode. Studies indicate a 40 percent improvement in weight for the fibrous nickel electrode over SOA electrode. Electrochemical impregnation of the Fibrex mats, from an aqueous bath of nickel nitrate-cobalt nitrate, yields loading levels comparable to SOA electrodes.

The major performance change of the Fibrex electrodes during cycling is the decrease of the high rate discharge capability rather than the decrease in the total capacity. The decrease in average pore size of the SOA sintered electrode results in poor electrolyte distribution in the Ni-H₂ cell which could possibly be considered to be one of the major failure modes of the cell. The bimodal distribution of the cycled Fibrex electrode should reduce this problem.

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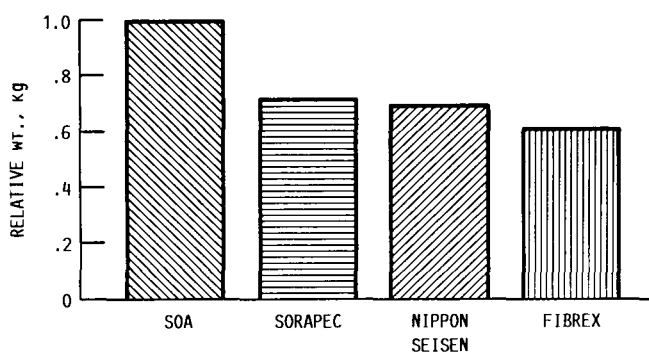


FIGURE 1. - RELATIVE WEIGHTS OF NICKEL ELECTRODES.

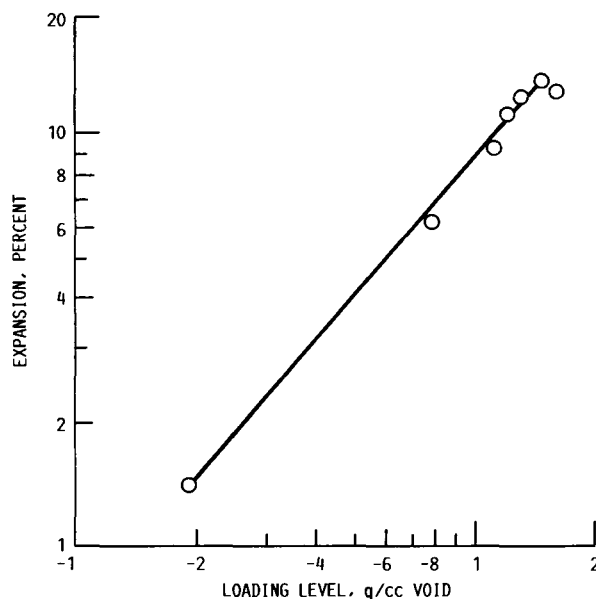


FIGURE 2. - LOG-LOG PLOT OF THE LOADING LEVEL VERSUS THICKNESS EXPANSION OF FIBREX ELECTRODE.

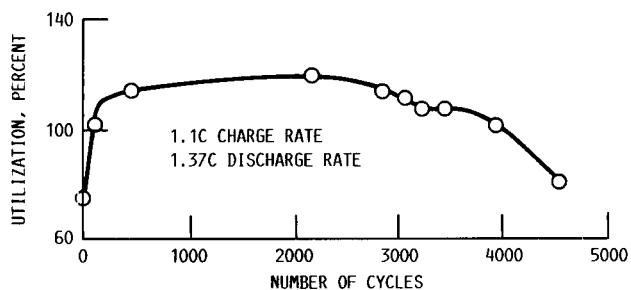


FIGURE 3. - CYCLE LIFE DATA OF FIBREX NICKEL ELECTRODE.

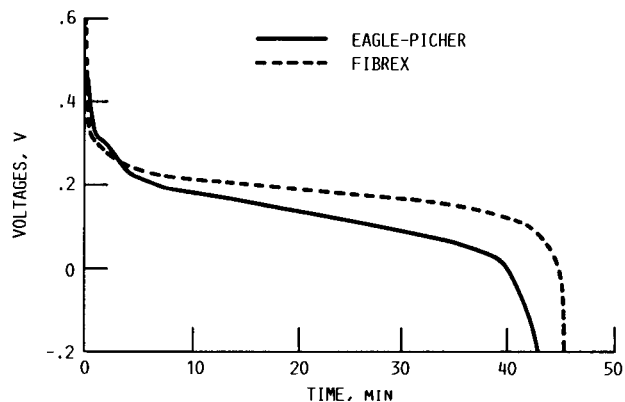


FIGURE 4. - DISCHARGE CURVES OF FIBREX AND EAGLE-PICHER NICKEL ELECTRODES.

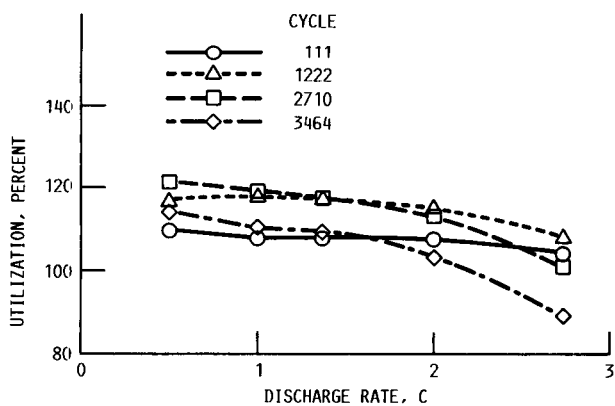


FIGURE 5. - UTILIZATIONS OF FIBREX NICKEL ELECTRODE AT VARIOUS DISCHARGE RATES.

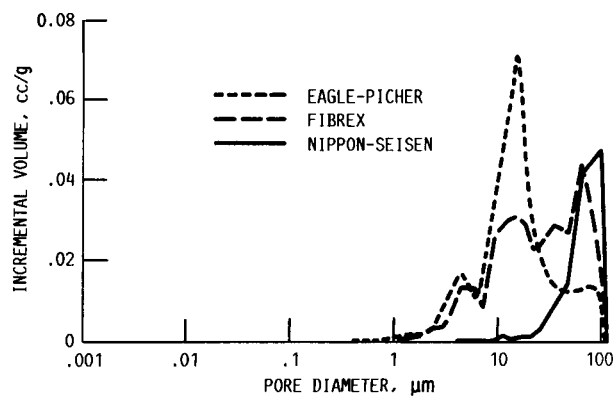
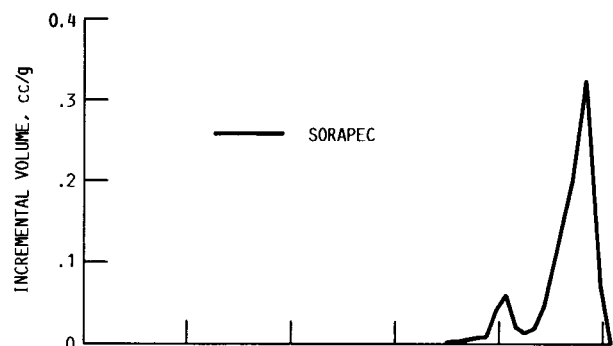


FIGURE 6. - PORE SIZE DISTRIBUTION CURVES OF NICKEL PLAQUES.

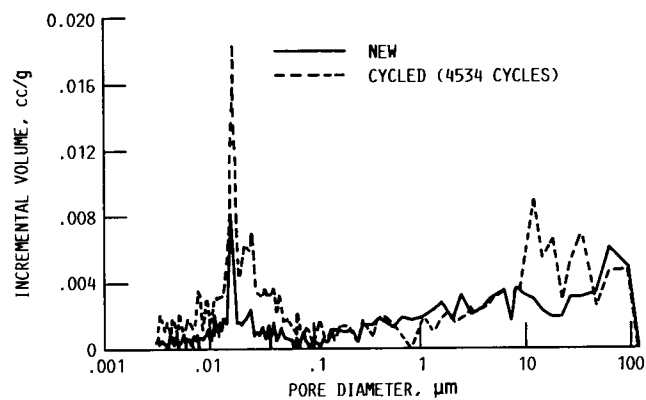


FIGURE 7. - PORE SIZE DISTRIBUTION CURVES OF FIBREX NICKEL ELECTRODE.

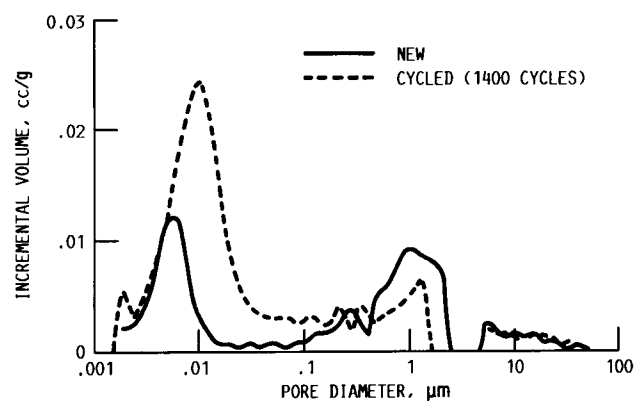


FIGURE 8. - PORE SIZE DISTRIBUTION CURVES OF EAGLE-PICHER NICKEL ELECTRODE.

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